Natural Sources of Gaseous Pollutants in the Atmosphere

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Abstract

Various gaseous pollutants including ozone, nitrous oxide, nitric oxide, nitrogen dioxide, methane, hydrogen, formaldehyde, ammonia, hydrogen sulfide, mercaptans, chlorine compounds and free radicals can be formed by natural processes such as ultraviolet photochemical processes in the upper atmosphere and microbiological processes. The modes of formation and destruction of these gases, especially of their concentrations in the atmosphere, and the various reactions in which these gases can participate with each other are discussed in detail.

I. Introduction

The concentration of pollutants within a given political or geographical urban area can arise (1) from combustion or industrial process sources within a given area, (2) from similar sources outside the boundaries of that area or, (3) from natural processes taking place over large areas of the earth's surface or upper atmosphere. The pollution arising from man-made sources outside a given area may come from nearby cities or industrial areas. But the pollutants may also come from distant sites not at all obvious, and perhaps only occasionally offenders, under special meteorological conditions.

Even if all man-made sources of pollution could be completely eliminated, concentrations of many natural pollutants would remain. These concentrations therefore represent the lowest possible concentrations of pollutants achievable with perfect air pollution control devices. These natural concentrations also can be of some importance in the calibration of air pollution instruments. Since many of these gaseous pollutants react with each other and undergo photolysis in the presence of sunlight, the discussion of these reactions is necessary fully to appreciate the overall situation regarding gaseous pollution.

The gaseous pollutants are generally in the range below 100 parts per million and, excepting carbon monoxide, the individual gases exist at no more than several parts per million and usually in considerably lower quantities. The major atmospheric gases, including nitrogen, oxygen, argon, water vapor and carbon dioxide, are excluded from this discussion. It is, of course, true that at high altitudes, in the midst of severe fires or during volcanic eruptions, the concentration of major atmospheric gases may be so affected as to result in a situation detrimental to health and often to life. However, such situations are not of concern from the urban pollution standpoint. Therefore, the gases which constitute possible hazards to the health of the community are generally present in almost insignificant amounts from the usual viewpoint. These gaseous pollutants may be taken as identical with the trace gases in the atmosphere if we exclude helium, neon, krypton, and xenon from discussion because of their chemical inertness.

The major natural processes which can result in gaseous pollutants include ultraviolet photochemical reactions in the upper atmosphere, microbiological reactions and the escape of gases from openings in the earth's surface. Minor natural processes include such sources as lightning strokes and the forest fires they may cause. The gases known to be produced by such processes in measurable amounts include ozone, nitrous oxide, methane, and hydrogen. Very small quantities of nitric oxide and nitrogen dioxide, formaldehyde, ammonia, hydrogen sulfide and mercaptans and gaseous chlorine compounds should be present in the atmosphere as a result of natural processes. Interesting also are the small but important amounts of free radicals involved in upper atmosphere photochemical reactions. Sulphur dioxide and iodine are not discussed since only man-made sources of pollution appear to exist.

It is important to note that ultraviolet radiation plays a significant role in natural processes as it does in some urban pollution situations. As a consequence, the types of reactions, reaction rates, and the concentrations of reactant and product gases most certainly differ in a complex fashion between day and night.

In the following sections, the methods of production, destruction, and the concentrations of the various individual trace gases will be discussed. It will be obvious that the information available varies widely from gas to gas. Since ozone is quite possibly the most important trace gas and also the one about which we have the most information, it will be discussed first.

II. Ozone

Ozone is by far the most important natural trace constituent of the atmosphere. It is formed almost exclusively by photochemical reaction in the upper portion of the ozonosphere (above 20 or 30 km.). In the Runge-Schumann continuum below 1750A, it is accepted that ozone is formed by the following reactions (VOLMAN, 1956a; BRINER, 1956)

$$O_2\,(^3\Sigma_g^-) \rightarrow O\,(^3P) + O\,(^1D)$$

where O (^{3}P) is the ground and O (^{1}D) an activated state, ozone is then formed by the three-body reaction

$$O_2 + O + M \rightarrow O_3 + M$$

where M is the third body.

The Runge-Schumann banded structure exists between 1760 and 1925A. Ozone is produced by irradiation from 1750 to 2000 or 2100A at atmospheric pressure (BRINER, 1956). The formation of ozone in this region apparently involves the transition $O_2(^3\Sigma_g^-) \rightarrow O_2(^3\Sigma_u^-)$ followed by the reactions (VOLMAN, 1956a, 1956b; FLORY, 1936)

$$O_2(^3\Sigma_u^-) \rightarrow O(^3P) + O(^3P)$$
$$O_2 + O + M \rightarrow O_3 + M$$

An alternative mechanism which has been proposed involves O_4 molecules (BRINER, 1956)

$$O_4 \rightarrow O_3 + O(^1D)$$

followed by the three-body reaction given already.

There appears to be considerable evidence for O_4 at high oxygen pressures and in liquid oxygen (LEWIS, 1925; WULF, 1927). The O_4 molecule has a continuous absorption band to 2400A and band spectra to above 2550A (WULF 1927). Ozone is formed from oxygen at high pressures with 2530A radiation. However, at atmospheric pressure, only about 0.03 percent O_4 would exist (LEWIS, 1925) and at the pressures in the upper ozonosphere a very negligible amount of O_4 would be present.

The ozone formed is itself photolyzed beginning at about 3500A by the reaction

$$O_3 \rightarrow O_2(^3\Sigma_g^-) + O(^1D)$$

Ozone also is decomposed by reaction with atomic hydrogen above 70 km. Section IX. In the lower atmosphere near ground level, ozone is decomposed by reaction with gaseous organic molecules associated with urban pollution, particulate matter, and with vegetation.

Ozone appears unique in its formation of stratified layers in the atmosphere (GÖTZ, 1951). The primary layer is formed at 20 to 30 km. high (PAETZOLD, 1955), but at times a secondary layer is found at 10 to 20 km and a tertiary layer at about 5 km up in the troposphere (PAETZOLD, 1955). Balloon observations at Weiszenau (48° N) and in Greenland show ozone maxima (cm O_3/km) at 23 km, 15 km, and 6 km. The maxima at 15 km and 6 km appear in the spring and disappear in the fall of the year.

The portion of total ozone above a given altitude drops rapidly with increasing altitude. About 90 percent of the atmospheric ozone

is below 35 km, 99 percent is below 45 km, and 99.9 percent below about 55 km. (JOHNSON ET AL., 1952).

The ozone concentration in the ozone layer between 20 and 30 km reaches 5 to 10 parts per million by volume. In the tertiary layer in the troposphere the ozone concentration reaches 0.1 to 0.2 parts per million by volume. In most locations near the earth's surface the ozone drops down to 2 or 3 parts per hundred million by volume. This value of 2 or 3 pphm by volume has been confirmed by infrared (TAYLOR and YATES, 1956, 1957; BIRKELAND, ET AL., 1957), ultraviolet (BAUM and DUNKELMAN, 1955; STAIR, ET AL., 1954), and chemical measurements (HAAGEN-SMIT, 1955) in locations distant from industrialized urban centers.

The total amount of ozone in 1 cm^2 column can be as much as 4 mm (NTP) (DOBSON, 1950). Usually, the total ozone is near 2 mm (NTP) (JOHNSON, ET AL., 1951, 1952). The total ozone concentration through the atmosphere shows variations dependent on the season of the year and on the latitude of observation (GÖTZ, 1951; DOBSON, 1950). The ozone appears to peak in the early spring and declines to its minimum value in the late fall and early winter months in both hemispheres (DOBSON, 1950). The seasonal variation in ozone concentration can be as great as 60 percent (DOBSON, 1950). The total ozone minimizes at the equator, reaches a value about 50 percent higher at 60° N and 60° S and drops off again at higher latitudes (GÖTZ, 1951). The variation with latitude is more marked in the spring than the autumn.

Significant changes in ozone concentration with the movement of weather fronts have been reported (STAIR, ET AL., 1954; DOBSON, 1950). Such variations have been observed in ground level measurements of ozone on the North American continent (STAIR, ET AL., 1954) and in total atmospheric ozone over the continent of Europe.

Relatively little data is available on nighttime ozone concentrations. A substantial increase in ozone has been measured during the night hours with much of the increase occurring right after sunset. A corresponding decrease at sunrise also was noted (RAMANATHAN and MURTHY, 1953).

Several different theories have been advanced to account for the ozone concentrations found in the troposphere. Probably the most widely accepted theory proposes that the ozone in the lower atmosphere results from downward transport from the upper atmosphere. A second theory suggests that the ozone in the troposphere is formed by electrical disturbances (CAUER, 1954). Finally, it has been proposed that the ozone near the surface actually is the result of photolytic reactions involving urban pollutants as in the Los Angeles area. It would seem probable that all three processes could contribute to the total ozone content.

This brief discussion of atmospheric ozone does not presume to cover completely all the aspects of this subject. More complete reviews are available elsewhere (GÖTZ, 1951).

III. Nitrogen Oxides

A. Nitrous Oxide

Both infrared (ARNOLD, 1954) and mass spectrographic (TAYLOR, ET AL., 1948) and combustion (KRIEGEL, 1944) analyses have shown that nitrous oxide is evolved in appreciable quantities from soils under anearobic conditions. The infrared analyses were performed both on laboratory soil samples and in the field (ARNOLD, 1954). Poorly aerated soils which are approaching saturation with moisture rapidly release large amounts of their available nitrogen as nitrous oxide.

It has also been proposed that nitrous oxide is formed by the reaction of molecular nitrogen with ozone in the ozonosphere (about 10 to 45 km) and at ground level by the following reactions (HARTECK and DONDES, 1954a):

$$N_2 + O + M \rightarrow N_2O + M$$

where M is a third body, and

$$N_2 + O_3{}^{\star} \rightarrow N_2O + O_2$$

where $O_3{}^{\star}$ is an activated ozone molecule. The laboratory kinetic data available (HARTECK and DONDES, 1954b) indicate that a slow reaction does occur between ozone and nitrous ozide. Similarly, the reaction of molecular nitrogen and atomic oxygen can occur in the upper atmosphere above 80 km where relatively large atomic oxygen concentrations are available. Above about 45 km, little ozone is available for reaction since the frequency of ozone-forming collisions decreases much more rapidly

with increasing altitude than does the molecular oxygen concentration.

Nitrous oxide would be destroyed by photolysis owing to radiation below 2100A (ZELIKOFF and ASCHENBRAND, 1954; ZELIKOFF, ET AL., 1953), by the following reactions:

$$N_2O \rightarrow N_2 + O$$
$$O + N_2O \rightarrow 2NO$$
$$O + N_2O \rightarrow N_2 + O_2$$
$$O + O + M \rightarrow O_2 + M$$

Radiation of this wavelength would penetrate to the top of the ozonosphere.

The presence of nitrous oxide in both the upper atmosphere and at ground level and of world-wide distribution has been confirmed by infrared (ADEL, 1939, 1951a, 1952; SHAW, ET AL., 1948, 1951, 1952; MIGEOTTE, 1948; MCMATH and GOLDBERG, 1949; GOLDBERG and MÜLLER, 1953) and mass spectrographic methods (SLOBOD and KROGH, 1950). All three nitrous oxide infrared bands have been identified (ADEL, 1952). There is no indication of a layer or layers in the region above about 15 km (GOLDBERG and MÜLLER, 1953). Some results suggest a greater concentration of nitrous oxide near ground level (ADEL, 1951). The amount of nitrous oxide at ground level as determined by mass spectrographic analysis is 0.5 ($\pm$0.1) ppm by volume (SLOBOD and KROGH, 1950). Recently, ground level infrared measurements over long path lengths have been analyzed (TAYLOR and YATES, 1956; BIRKELAND, ET AL., 1957) giving N_2O concentrations of 0.5 ($\pm$0.1) ppm which is in excellent agreement with the mass spectrographic result. However, ground level infrared measurements made at Columbus, Ohio gave concentrations of only 0.28 ppm by volume (BIRKELAND and SHAW, 1957). If nitrous oxide is the result of microbiological processes (see below), then it would not be surprising if its concentration varied with location and with season of the year.

The infrared measurements of the solar spectrum show a total of around 3 mm of nitrous oxide at NTP (KUIPER, 1952). This is about the same total concentration as that of ozone in the atmosphere.

Rough calculations indicate that the release of nitrous oxide by the soil can account for the concentration of nitrous oxide observed in the atmosphere (ARNOLD, 1954; GOODY and WALSHAW, 1953). The infrared results appear to favor evolution of nitrous oxide by the soil as the major source of nitrous oxide in the atmosphere (ADEL, 1951; GOODY and WALSHAW, 1953). However, more information on the vertical distribution of nitrous oxide would be highly desirable. More data on the kinetics of the nitrogen-atomic oxygen and nitrogen-ozone reactions are needed also.

B. Nitric Oxide and Nitrogen Dioxide

Little is known about the formation of nitric oxide and nitrogen dioxide from natural sources. The presence of measurable quantities of the other nitrogen oxides such as N_2O_3, N_2O_4, and N_2O_5 in the atmosphere seems doubtful.

It has been established that nitric oxide (and nitrogen dioxide by air oxidation) is formed under anaerobic conditions in silos containing corn, alfalfa, and cabbage (LOWRY and SCHUMAN, 1956; PETERSON, ET AL., 1956). Several hundred parts per million of nitrogen dioxide have been detected in silos immediately after storage of silage (LOWRY and SCHUMAN, 1956). The process apparently involves the reduction of nitrates to nitrites by forage bacteria (PETERSON, ET AL., 1956). The nitrites are converted to nitrous acid which breaks down to nitric oxide. Just how widespread such bacteriological processes are on the earth's surface is difficult to estimate. Measurements for nitric oxide of soil samples under various experimental conditions would be most desirable.

Some nitric oxide also can be formed in the upper atmosphere through the photolysis of nitrous oxide. Laboratory experiments indicate that about 5 to 10 percent of nitric oxide is formed upon photolysis of nitrous oxide at 1850A (and up to 2000A) probably by means of the following reactions (ZELIKOFF and ASCHENBRAND, 1954):

$$N_2O \rightarrow N_2 + O$$
$$O + N_2O \rightarrow 2NO$$

From the second reaction it is evident that nitric oxide could be formed by direct attack of atomic oxygen on nitrous oxide at altitudes above about 80 km.

Nitrogen molecules can be ionized and dissociated by ultraviolet radiation below 800A

and by the X-ray bombardment (BRYAM, ET AL., 1954) in the E-layer above 100 km (NICOLET, 1955a). Nitric oxide can then be formed by the reaction

$$N + O + M \rightarrow NO + M$$

Small amounts of nitric oxide are also formed by electrical storms.

Theoretical consideration of the formation of the ionized D layer in the ionosphere (80—100 km) indicates that the process

$$NO + h\nu \rightarrow NO^+ + e^-$$

could well account for the major portion of the ionization assuming approximately 10^{18} molecules/cm. (BATES and SEATON, 1950; MITRA, 1954; NICOLET, 1955a). Recent measurements of the radiation from nitric oxide release from a rocket at about 95 km indicate that an artificial ion cloud is formed (MARMO, 1956). The results are claimed to be compatible with the formation of the D layer by the action of solar Lyman alpha radiation upon nitric oxide (BATES, 1952; MARMO, 1956). The twilight and night air glow also may be due to the $NO + O \rightarrow NO_2$ reaction (NICOLET, 1955b; PRESSMEN, 1956), or to the $N + O_3 \rightarrow NO + O_2$ (BARTH and KAPLAN, 1957).

No certain indication of any fine structure due to the nitric oxide fundamental in the infrared has been found (SHAW, 1951a, 1952; MIGEOTTE and NEVEN, 1952); consequently, there are presumably less than 5×10^{17} molecules/cm^2 (MIGEOTTE and NEVEN, 1952). Theoretical calculations result in estimates that there are 10^{11} to 10^{12} molecules/cm^3 at 80 km. (NICOLET, 1955a; MITRA, 1954; BATES and SEATON, 1950). Positive-ion and negative-ion spectrographs flown in a rocket showed NO_2^+ from 93 to 131 km during daylight (JOHNSON and HEPPNER, 1956). A mass 46 peak probably due to NO_2 was detected between 88 and 80 km with a neutral gas spectrometer (MEADOWS and TOWNSEND, 1956).

Chemical measurements of nitrogen dioxide at remote sites in Florida and Hawaii give values between 0.1 and 1 pphm (JUNGE, 1956, 1958).

All of the evidence to date appears to indicate that nitric oxide and nitrogen dioxide are present in the atmosphere from natural sources but at concentrations of a few pphm or less.

Since nitrogen dioxide is readily photolyzed by light beginning above 4000A, it is dissociated down to ground level. During daylight the NO_2 concentration should be much less than that of nitric oxide (BATES and SEATON, 1950; MITRA, 1954; NICOLET, 1955b). At night the nitrogen dioxide concentration should build up rapidly by reaction of nitric oxide with atomic oxygen and ozone. Above 100 km the reaction of atomic nitrogen with oxygen might be a source of nitrogen dioxide. During the night the amount of NO_2 may exceed that of NO in certain portions of the atmosphere, especially the ozone layer (NICOLET, 1955a).

IV. Hydrocarbons

Hydrocarbons have been reported in urban atmospheres to concentrations as high as 1 to 2 ppm (LITTMAN and DENTON, 1956). Many of these materials are gasoline fraction hydrocarbons from automobile exhausts and petroleum storage facilities. Incineration produces appreciable quantities of lower molecular weight hydrocarbons. The total hydrocarbon present includes paraffins, olefins, alkynes, some aromatics, and probably small amounts of cyclics and diolefins.

In contrast, the natural sources of hydrocarbons produce a much smaller range and variety of hydrocarbon species. In fact almost all natural processes produce methane as their major if not their sole constituent. Olefins are produced in extremely small quantities by natural processes with only one source in which they predominate. Aromatics, alkynes, and diolefins appear to result only in trace amounts from natural sources. It has been well established that methane is the principal hydrocarbon product of anaerobic bacterial fermentation of sewage (BUSWELL and MUELLER, 1952; GROSSE and LIBBY, 1948). Ethane, ethylene, acetylene, etc. are reported at concentrations between 7 and 0.1 ppm by volume (BUSWELL, 1954). Bacterial organisms that cause this fermentation are almost universally found in nature and only methane, mineral oils, and lignins appear almost immune to attack (BUSWELL and MUELLER, 1952; BUSWELL, 1954). These processes also occur in swamps, marshes, ponds, lakes, etc. (DZENS-LITOVSKIY, 1945). The total contribution of methane to the atmosphere from these diverse sources is estimated to amount to 10^7 to 10^8 tons per year (HUTCHINSON, 1954).

Natural gases are used for fuel in the United States today in large quantities. In the past in the United States large quantities of natural gas were lost to the atmosphere and are lost even today elsewhere in the world. Natural gases contain about 36—97 percent methane, 1—25 percent ethane, 1—17 percent propane, 1—17 percent butane, and small amounts of C_5 and C_6 paraffinic hydrocarbons (SACHANEN, 1945). The olefin content is extremely small. Use of the tomato plant, a very sensitive biological indicator of ethylene, showed only 0.001 percent ethylene in a natural gas from Charleston, West Virginia (CROCKER, 1932). Only traces of aromatics are to be found in natural gases (SACHANEN, 1945).

Appreciable amounts of methane are found in coal mines as the so-called firedamp. A small amount of ethane in mine gases has also been claimed (VAN TIGGELEN, 1945; BUREAU OF MINES, 1938).

Ethylene is produced by growing plants, fruits, roots, and tubers. However, the concentrations are in the ppm range and below (ZIMMERMAN, 1952). Traces of cyclics such as terpenes also have been reported. Owing to the low initial concentrations, growing vegetation should not make any appreciable contribution to the natural hydrocarbon content of the atmosphere.

The presence of methane in the earth's atmosphere at many diverse locations has been shown by means of infrared measurements with grating instruments of the solar spectrum (MIGEOTTE, 1948a, 1948b; ADEL, 1949; GOLDBERG, 1951; NIELSON and MIGEOTTE, 1952; GOLDBERG and MUELLER, 1953). Methane is a permanent constituent of the atmosphere of world-wide distribution. Infrared observations further show that methane is uniformly mixed with the major constituents of the atmosphere (GOLDBERG and MUELLER, 1953). The concentration of methane is about 2 ppm or 1.2 cm NTP (GOLDBERG and MÜELLER, 1953). On the other hand, the methane found in the krypton-xenon fraction of the air amounts to about 1.2 ppm (GLUECKAUF, 1951). Despite attempts to detect some details of the rotation-vibrational fine structure of ethylene and ethane, no success has been reported in finding traces of these gases in the earth's atmosphere (SHAW and CLAASSEN, 1952; SHAW, ET AL., 1951, 1952). The absence of any evidence for ethylene in the infrared indicates that much less than 0.01 cm NTP is present (GOLDBERG and MUELLER, 1953). Considering the extremely small quantities of ethylene produced from natural sources, it is doubtful that the quantities present, which are probably below the ppb range, will be detectable. If the contribution from natural gas leakage made up a major portion of the total, the fine structure of ethane, propane, and butane vibrational bands should be detectable. It seems more likely that natural gas leakage contributes no more than a few percent of the total hydrocarbons lost by all sources to the atmosphere. Consequently, the C_2—C_4 saturated hydrocarbons would be present at two or three orders of magnitude less than methane. In agreement with this estimate, the infrared determinations indicate that these hydrocarbons, if present, must be at least two orders of magnitude in concentration less than the methane (SHAW, ET AL., 1951, 1952).

It should be noted that the concentration of methane observed in the general atmosphere of the earth is as high as the total hydrocarbon concentrations reported over the large cities of California. Some care must be taken that the presence of this natural background concentration of methane is corrected for in making measurements of urban hydrocarbon concentrations. For example, if a non-dispersive infrared analyzer is being used to dertermine hydrocarbon concentrations, no difficulty will be encountered if the calibration mixture is made up in air. If the calibrating hydrocarbon, say hexane, is mixed with nitrogen instead of air, an error will result. The total concentration read on the instrument would be the sum of natural methane plus gasoline fraction hydrocarbons. Since the sensitivity of the response of the instrument to methane may be about one-fifth that of hexane (LITTMAN and DENTON, 1956), 2 ppm of methane would be the equivalent of about 0.4 ppm of hexane.

From the standpoint of reaction rates of gaseous pollutants, the fact that the natural background concentration of hydrocarbon consists almost entirely of methane is of importance. The rate constants for a second order reaction between hydrocarbons and ozone have been determined recently for both paraffinic and unsaturated hydrocarbons (CADLE and SCHADT, 1952; SCHUBERT and PEASE, 1956). At room temperature, the rate constant for

methane is 0.85 cc/mole-sec. while that of ethylene is 1.9×10^6 cc/mole-sec. Consequently at equal concentrations of methane and ethylene, the rate of reaction of ethylene with ozone is about 2×10^6 times as rapid as of methane with ozone. Therefore, while the time for half reaction of the hydrocarbon and ozone at 1 ppm is only several hours for the ethylene-ozone reaction, the time for half reaction for the methane-ozone reaction is of the order of 10^4 years. Obviously, then methane in the atmosphere does not take part in the destruction of ozonosphere or ground level ozone. Other reaction processes cause much more rapid destruction of the ozone. It should be noted that there are some claims in the literature that atomic oxygen does react appreciably with methane; however, in at least part of this work (ARRAMENKO and KOLESNIKOVA, 1953), the atomic oxygen was obtained by the dissociation of water vapor in which case atomic hydrogen is also likely to form (STEACIE, 1946a). The atomic hydrogen tends to accelerate the reaction through formation of a reactive intermediate other than atomic oxygen or ozone (HARTECK and KOPSCH, 1931; GEIB and HARTECK, 1934). This reaction with atomic hydrogen will be discussed in more detail below.

Using a figure of 3.2×10^9 molecules/cm^2 of CH_4 over the earth's surface (GOLDBERG and MUELLER, 1953), one can calculate at total weight of CH_4 in the earth's atmosphere of 4.4×10^9 metric tons. Thus, with an output of CH_4 of 10^7—10^8 tons per year from natural sources, if the earth's atmospheric supply of methane is not increasing, the supply is being completely replenished every 40 to 400 years. If equilibrium is to be maintained, processes for the destruction of methane must be available.

Methane can be photolyzed below 1450A (NOYES and LEIGHTON, 1941a) in the upper atmosphere. The strongest source of radiation in this region is the Lyman α band at 1216A which penetrates to 70 km. (TOUSEY, 1953), that is, to about the bottom of the D layer of the ionosphere. Since the weaker radiation between the Lyman α and 1450A probably does not penetrate below 70 km. (FOSTER, 1951), photolysis can occur only by the upward passage of the methane from the earth's surface through the troposphere and the ozonosphere into the D and E layers of the ionosphere. The photolysis of methane will produce some higher molecular weight hydrocarbons (NOYES and LEIGHTON, 1941) probably by the following reactions:

$$CH_4 + h\nu (< 1450A) \rightarrow CH_3^{\cdot} + H^{\cdot}$$
$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6$$
$$CH_3^{\cdot} \rightarrow CH_2^{\cdot} + H^{\cdot}$$
$$CH_2^{\cdot} + CH_2^{\cdot} \rightarrow C_2H_4 \text{ etc.}$$

However, these hydrocarbons also undergo photolysis to reform methane at even longer wavelengths (>1450A), so they will be rapidly destroyed again.

It has already been pointed out that the reactions of ozone and atomic oxygen with methane apparently are very slow, so that destruction of methane cannot occur by means of these reactions alone in the ozonosphere and ionosphere. However, it has been shown in the laboratory that in the presence of hydrogen atoms a mixture of methane and oxygen undergoes rapid reaction even at —183° C (GEIB and HARTECK, 1934).

In the upper atmosphere above the ozonosphere, water vapor can be photolyzed in the following reaction:

$$H_2O + h\nu (< 1800A) \rightarrow H^{\cdot} + OH^{\cdot}$$

The atomic hydrogen can then react with molecular oxygen to form the perhydroxy radical:

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$

This free radical then attacks the methane molecule:

$$HO_2^{\cdot} + CH_4 \rightarrow \text{oxidation products}$$

The first step of the reaction may be hydrogen abstraction:

$$HO_2^{\cdot} + CH_4 \rightarrow CH_3 + H_2O_2$$
$$CH_3^{\cdot} + HO_2^{\cdot} \rightarrow CH_2^{\cdot} + H_2O_2$$

The methyl and methylene radicals could then react with atomic oxygen to form the methoxy radical and formaldehyde:

$$CH_3^{\cdot} + O^{\cdot} \rightarrow CH_3O^{\cdot}$$
$$CH_2^{\cdot} + O^{\cdot} \rightarrow CH_2O$$

Reaction with molecular oxygen and ozone at the top of the ozonosphere might also occur. One would expect formaldehyde as an intermediate which could either be further oxidized

or readily photolyzed. Some higher molecular weight hydrocarbons might also be formed by radical recombination processes, but these hydrocarbons would be photolyzed also, as mentioned previously. All of the radical recombination processes may occur slowly owing to the very low concentration of radicals and third bodies in the upper atmosphere.

The other possible method of destruction of methane is by means of methane oxidizing bacteria (FOSTER, 1951). Unfortunately, little appears to be known about this type of bacteria. Since, as previously pointed out, common fermentative bacteria do not break down methane (BUSWELL and MUELLER, 1952), bacterial action at present does not appear as a major process for its destruction.

V. Hydrogen

Hydrogen has been reported in trace amounts in volcanic (NIGRO, 1939), and in natural gases (<0.05 mole percent) (BREWER and DIBELER, 1945). Appreciable amounts of hydrogen are formed under certain conditions in the bacterial fermentation of carbohydrates (BUSWELL and MUELLER, 1952). Among the types of bacterial fermentation resulting in hydrogen are the fermentation of carbohydrates by the *coli-aerogenes* group of bacteria, the butanol-acetone fermentation, and the fermentation of pyruvic acid and certain amino acids by clostridia (KOFFLER and WILSON, 1951; BUSWELL, 1954). Hydrogen is formed in the upper atmosphere by photolysis of water vapor as has been mentioned previously. Hydrogen may also enter the earth's atmosphere as proton streams from the sun.

Hydrogen can readily escape out of the earth's atmosphere (SPITZER, 1952). The hydrogen content of the upper atmosphere, 100—300 km, is greater than in the lower atmosphere but even at these altitudes hydrogen is not a dominant species (SPITZER, 1952).

Many bacteria can utilize hydrogen as an energy source for the synthesis of protoplasm. Hydrogen is utilized by some of these species in such a way as to reduce nitrite and amino acids (KOFFLER and WILSON, 1951).

Some of the hydrogen formed by the photolysis of water vapor is removed by reaction with ozone (MCKINLEY and GARVIN, 1955) and atomic oxygen or molecular oxygen (NOYES and LEIGHTON, 1941).

Only a small amount of information on the hydrogen concentration of the atmosphere is available, since hydrogen does not absorb as a dipole in the infrared nor in the ultraviolet until far into the vacuum ultraviolet. A few analyses indicate a hydrogen concentration of about 0.5 ppm by volume, or 0.4 cm. NTP (GLUECKAUF, 1951).

VI. Formaldehyde

It has been shown in the laboratory that if a mixture of carbon dioxide and water is photolyzed with the radiation from a Xenon lamp (1470A and 1295A) some formaldehyde is formed (GROTH and SUESS, 1938; NOYES and LEIGHTON, 1941). A similar reaction can occur above 70 km. in the atmosphere. Formaldehyde possibly may also be formed in the reaction between oxygen and methane in the presence of hydrogen atoms. However, the formaldehyde so formed would be subject to further attack by atomic oxygen to form carbon monoxide, hydrogen, and carbon dioxide. Also, the formaldehyde produced will be photolyzed by radiation up to 3600A (NOYES and LEIGHTON, 1941). This means that formaldehyde is subject to photolytic decomposition throughout the atmosphere down to ground level. Formaldehyde may also be formed from carbon dioxide and water during electrical storms as a result of electrical discharges.

Formaldehyde has been detected qualitatively by chemical methods in rainwater collected in remote sites including one at high altitudes (DHAR and RAM, 1932). Estimates of formaldehyde existing throughout the atmosphere at less than 1 mm. NTP have been made (CHAPMAN, 1951). However, no infrared or ultraviolet identification of formaldehyde in the atmosphere appears to have been made. A mean value of 0.5 micrograms/meter^3 for formaldehyde on the mainland of Europe has been reported (CAUER, 1951).

VII. Carbon monoxide

No bacteriological sources of carbon monoxide appear to exist (FOSTER, 1951). Carbon monoxide has not been reported as present in natural or volcanic gases (SACHANEN, 1945). While carbon monoxide is found in coal gases, most of it must result from mining operations and not natural processes. Some carbon monoxide must be formed in the upper atmosphere

above 70 km by the reaction (NOYES and LEIGHTON, 1941).

$$CO_2 + h\nu (< 1700) \rightarrow CO + O$$

The reports on atmospheric carbon monoxide as observed with grating infrared solar measurements differ from those for ozone, methane, and nitrous oxide. One group of observers has been unable to find carbon monoxide above their stations of observation (GOLDBERG, 1952). In one case, observations made at the Jungfraujoch mountain observatory in Switzerland show five-fold changes in concentration of carbon monoxide and appreciable fluctuations in even one hour (BENESCH, ET AL., 1953). The concentrations in cm-atmos. ranged from 0.017 to 0.075. Similarly, observations in Ottawa showed variations between 0.09 to 0.18 cm-atmos. (LOCKE and HERZBERG, 1953). These variations suggest that while a small part of the total atmospheric carbon monoxide may result from upper atmosphere processes, most of the atmospheric carbon monoxide results from man-made emissions. The fluctuations are probably the results of packets of air from urban centers passing over the observation stations.

VIII. Hydrogen Sulfide and Mercaptans

Hydrogen sulfide is usually present at very low concentrations in natural gases but some natural gas deposits contain as much as 5 to 10 percent (SACHANEN, 1945). Traces of hydrogen sulfide also are found in volcanic gases (NIGRO, 1939; SICARDI, 1940). Small amounts of H_2S are formed from microbiological reactions involving the breakdown of the amino-acid cysteine by *E. coli* and other organisms. However, the major biological source of H_2S probably is the *sporovibrio desulfuricans* which utilize sulfates to produce H_2S. Methyl mercaptan is formed by the attack of *E. coli* on methionine.

No chemical measurements of hydrogen sulfide at remote locations appear available. Infrared fine structure bands due to H_2S have not been observed. However, hydrogen sulfide is a weak absorber in the infrared region.

IX. Ammonia

Ammonia is liberated from protein waste materials through deamination processes by enterobacteriaceae and clostridia organisms. While the deamination mechanisms vary, most amino acids are decomposed to give ammonia by one mechanism or another (GALE, 1951). Ammonia is not found generally in natural, volcanic or mine gases (SACHANEN, 1941; NIGRO, 1939; SICARDI, 1940). No photochemical processes appear available by which ammonia could be formed in the upper atmosphere.

Attempts to find infrared fine structure for ammonia in the 10.55 micron band have been unsuccessful (SHAW, ET AL., 1951, 1952). Extensive analyses of ammonia in rainwater falling at many locations in Scandinavia indicate average concentrations of only 2 to 4 micrograms/meter^3 which would correspond to only a few parts per billion of ammonia (EGNER and ERIKSSON, 1955). Other data obtained on the mainland of Europe give average concentrations of 8 micrograms/meter^3 (CAUER, 1951). Determinations of NH_3 and NH_4^+ in Florida gave average values of 5 micrograms/meter^3 and those in Hawaii gave only 2.5 micrograms/meter^3 (JUNGE, 1956, 1958). Even if all of the material were in the form of NH_3 the concentration rarely exceeds 1 part per hundred million which is probably beyond the limit of detectability by the infrared method.

X. Chlorine Compounds

It is contended that the chlorides from seawater can be converted to chlorine, hydrogen chloride, and chlorine oxides (CAUER, 1951). This contention is based mostly on indirect evidence from analyses leading to ratios of chloride to cation, Cl^-/Na^+, Cl^-/K^+ and Cl^-/Mg^{+2}. However, gaseous chlorine has been reported at about 2 micrograms/meter^3 (JUNGE, 1958). The possibility also exists that moist sodium or potassium chloride particles react with nitrogen dioxide to form nitrosyl chloride (GRAY and YOFFE, 1955).

$$2NO_2 + NaCl \rightarrow NOCl + NaNO_3$$

In the presence of ozone nitrosyl chloride can be oxidized further to nitryl chloride NO_2Cl. Both compounds should readily photolyze back to nitric oxide, nitrogen dioxide, and chlorine (KISTIAKOWSKY, 1930). The best place to observe the presence of nitrosyl chloride, if it exists, would be in the Los Angeles area where the sea salt could come in contact with several tenths of a part per million of nitrogen

oxides. Analysis for NOCl in the infrared would be difficult since the very strong 5.6 micron band of nitrosyl chloride would be obscured by water vapor absorption.

XI. Free Radicals

A number of free radical species have been mentioned above. These include $OH^{\cdot}$, $HO_2^{\cdot}$, $CH_3^{\cdot}$, and $CH_2^{\cdot}$. Nitric oxide and nitrogen dioxide are also free radicals but are discussed separately because of their long lives and great importance. The sodium atom also is an atomic free radical, since it has an unpaired electron, and it is of considerable interest in upper atmosphere chemistry and physics.

A. Hydroxyl Free Radical, OH

The OH radical can be formed by a number of reactions in the upper atmosphere particularly at altitudes above 70 km. Among the reactions which may be involved are the following:

$$H_2O + h\nu(1800A) \rightarrow H^{\cdot} + OH^{\cdot}$$

$$H^{\cdot} + O_3 \rightarrow OH^{\cdot} + O_2$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$

$$HO_2^{\cdot} + H \rightarrow OH^{\cdot} + OH^{\cdot}$$

$$HO^{\cdot}{}_2 + H_2 \rightarrow H_2O + OH^{\cdot}$$

The OH radical can be destroyed by such reactions as the following:

$$OH + H + M \rightarrow H_2O + M$$

$$OH + OH \rightarrow H_2O_2$$

The vibration-rotation bands around 10,000A in the night sky have been proved to be due to the OH radical (MEINEL, 1950; HERMAN and HERMAN, 1955; JONES and GUSH, 1953; JONES, 1955). Observation of the 8347.6A band of OH indicates a winter maximum and a summer minimum in intensity (BERTHIER, 1955). Very little is known experimentally about the total concentration nor the variation of OH with height. Estimates of the height of the OH layer range from 70 to 300 km. The lower altitude seems more probable. Theoretical calculations give OH concentrations ranging from 5×10^7 molecules/cm^3 at 70 km, 5×10^6 molecules/cm^3 at 80 km, and 10^5 molecules/cm^3 at 80 km (BATES, 1954).

B. Perhydroxy Radical, HO_2

As pointed out formerly, the HO_2 free radical could be formed by the reaction of atomic hydrogen with molecular oxygen. This radical appears capable of readily oxidizing methane (GEIB and HARTECK, 1934). No spectroscopic evidence for this radical is available either in the atmosphere or the laboratory although the mass spectrum of HO_2 has been observed (FONER and HUDSON, 1953, 1955). Theoretical calculations give HO_2 concentrations about equal to those of OH with altitude.

C. Methyl and Methylene Radical, CH_3 and CH_2

The photodecomposition of methane can result in formation of the CH_3 and CH_2 radicals. No spectroscopic evidence for these radicals in the atmosphere is available, although the laboratory ultraviolet spectrum of the methyl radical has been observed recently (HERZBERG and SHOOSMITH, 1956).

D. Formyl Radical, CHO

Any formaldehyde present in the atmosphere would undergo at least partial photolysis to hydrogen atoms and CHO radicals. No spectroscopic evidence for the formyl radical in the atmosphere is available although the laboratory spectrum is well established (HERZBERG and RAMSAY, 1955).

E. Sodium Atoms, Na

Sodium atoms can occur in the upper atmosphere from sea salt or possibly volcanic particulate. The presence of sodium atoms in the upper atmosphere between about 70 and 100 km with maximum near 85 km is well established (ROBLEY, 1954; VEGARD, 1955; CHAMBERLEIN and MEINEL, 1954; DONAHUE, ET AL., 1956; KOOMEN, ET AL., 1956; MEADOWS and TOWNSEND, 1956). Concentrations of 10^9 and 10^{11} atoms/cm^2 in the region above 70 km appear to be in accord with the NaD line emission observed in the twilight and night sky (DONAHUE, ET AL., 1956). The sodium emission varies with the season in the same way as does hydroxyl free radical (BERTHIER, 1955; OMHOLT, 1956). Such processes as the following have been suggested to explain the

emission of sodium atoms in the night sky (CHAPMAN, 1951; OMHOLT, 1956):

$$Na + O + M \rightarrow NaO + M$$

or $$Na + O_3 \rightarrow NaO + O_2$$

$$NaO + O \rightarrow Na(^2Po) + O_2$$

XII. Conclusion

The above discussion indicates how very limited is our knowledge of the trace gases in the earth's atmosphere. Only for ozone and nitrous oxide do we have good information on the concentration and distribution in the atmosphere. Even in these instances the data are far from complete. Information on the variation N_2O concentration at altitudes at which photochemical decomposition occurs is lacking.

The limited data on ozone concentrations at locations remote from urban centers seem to indicate concentrations of only 2 or 3 ppm by volume. However, there is some very fragmentary information obtained at locations where strong downward movements of air from the upper atmosphere can occur. At such sites appreciable higher concentrations have been observed. Unfortunately, it is often difficult even at stations 50 or 100 miles from urban areas completely to rule out contamination from air masses flowing from the urban location. The ozone measurements to be made in the Antarctic during the International Geophysical Year should provide important data bearing on this problem.

There is still a discrepancy between the value obtained for the concentration of methane by infrared spectroscopy and that obtained from the heavy inert gas fraction of air. The total concentration of the higher paraffinic hydrocarbons may amount to several parts per hundred million. However, it will be exceedingly difficult to detect such small amounts by either optical or chemical methods.

Our knowledge of nitric oxide and nitrogen dioxide in the upper atmosphere is practically non-existent. Yet there is reason to believe that small concentrations of these gases must exist in our atmosphere. There are indications that NO and NO_2 are of importance in ionosphere phenomena in the D layer and in twilight and night air glow phenomena. It should be worth some effort to make measurements at remote sites at ground level and in the upper atmosphere. Colorimetric methods are available for the analysis of nitrogen dioxide and total nitrates. These methods should be adaptable, with sufficient effort, to upper air measurements.

Sensitive chemical methods are also available for formaldehyde and ammonia. These could probably be adapted to upper air determinations if the effort is justified.

Owing to the fact that carbon monoxide does not occur as a result of natural processes, it should be a sensitive indicator of the transport of urban pollution through long distances and into the upper atmosphere. Sufficient CO is present to permit determination by either infrared spectroscopy or chemical analysis.

The presence of free radicals such as $OH^{\cdot}$ and $Na^{\cdot}$ and possibly other radicals in the upper atmosphere from photochemical reactions is of considerable chemical interest. The question arises as to how far down into the lower atmosphere such radicals might be transported upon occasion. If such transport occurs, one may conjecture as to the possibility of such a free radical as OH participating in lower atmospheric reactions over urban areas.

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